DALTON
PERSPECTIVE

A net-based approach to coordination polymers†

Richard Robson

School of Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia

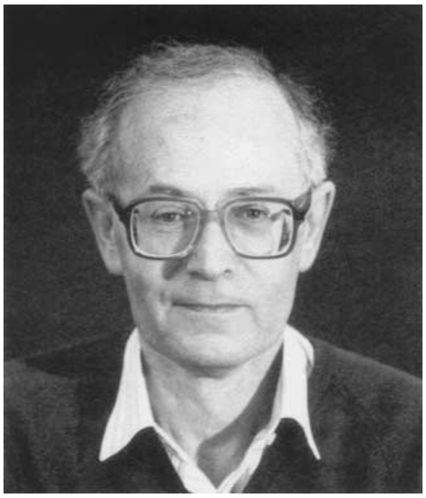
Received 4th May 2000, Accepted 23rd June 2000
First published as an Advance Article on the web 9th October 2000

True crystal engineering of coordination polymers with useful structure-based properties by design remains a distant prospect. The exploratory, experimental net-based approach to the construction of coordination polymers described in this article has provided a few examples of structures obtained by design, but also serendipitously revealed numbers of unprecedented and interesting structures that were totally unexpected. Further work with coordination polymers can confidently be expected to provide many similar surprises. It is proposed that carefully designed connecting ligands capable of binding metal centres strongly and predictably at chelating sites may afford improved structural control in network assembly and more robust network structures.

1 Introduction

No attempt is made in the following account to provide a comprehensive coverage of the now very extensive field of coordination polymers; rather, the net-based approach to infinite framework construction is described from a distinctly personal point of view, in-keeping with the style of Dalton Perspectives.

Dr Robson received both his BA and D Phil degrees from Oxford University. After post-doctoral work at the California Institute of Technology and at Stanford University he joined the staff of the then Department of Inorganic Chemistry at the University of Melbourne in 1966. A common theme in his research has been concerned with the imposition by design of some special organisation at the molecular level so as to achieve unusual structural or functional outcomes. In recent years his emphasis has been upon the design, synthesis and characterisation of infinite network structures.



Richard Robson

A net, which may be finite or infinite, is a collection of nodes with some clearly defined connectivity or topology. We are concerned here with infinite nets, many of which have concrete counterparts in the form of real chemical structures which provide convenient names for the nets. Other nets, some attractively simple, remain no more than abstract entities or are represented by only one or two real chemical structures. Wells has provided a most useful compilation of various nets of relevance to chemistry but no doubt many others await discovery.[1]

Simple examples of 2-D nets are the square grid and the hexagonal grid in which the centres are 4-connecting and 3-connecting respectively. Some of the simplest examples of infinite 3-D nets, which present themselves as realistic targets for the crystal engineer, are as follows: the α-polonium (or NaCl) net (with 6-connecting, octahedral centres); the diamond, Lonsdaleite, quartz, feldspar-related and zeolite-related nets (with 4-connecting, tetrahedral centres); the NbO net (involving square planar 4-connecting centres with a 90° twist along each connection); the PtS net (with equal numbers of tetrahedral and square planar centres); various 3-connected nets described by Wells,[1] the most symmetrical of which is the cubic (10,3)a net discussed further below; the rutile net (with octahedral and trigonal centres in 1:2 proportions); the "Pt_3O_4" net (with square planar and trigonal centres in 3:4 proportions) and the Ge_3N_4 net (with tetrahedral and trigonal centres in 3:4 proportions).

The approach we have adopted is based on the simple notion that if we can generate molecular building blocks with a functionality and stereochemistry appropriate to a particular one of the above target nets, then merely allowing these pre-organised components to react together under the correct conditions may lead to the spontaneous assembly of the intended network. Our experience and that of others suggests that the structural outcome of any particular framework building reaction may be determined by the subtle combination of a number of effects some of which may be quite weak, *e.g.* interactions in the crystal between the framework and solvate molecules which themselves may be highly dynamic. Outcomes therefore are to varying extents uncertain, but one can imagine that if a sufficient degree of pre-organisation is imprinted on the building blocks then the spontaneous assembly of the intended net may well become inevitable. It appears that at this stage theory falls very far short of being able to account for these weak but often structure-determining interactions and thereby to predict outcomes. Our approach is unashamedly experimental; it is based on chemical intuition and amounts to informed trial and error. Already it has revealed much new chemistry and there is every indication that it will continue to do so.

Metal–ligand bond formation provides a very convenient means of linking up components into infinite networks. Inorganic chemistry, in particular coordination chemistry, is replete with examples of easily accessible potential building

---

† Based on the presentation given at Dalton Discussion No. 3, 9–11th September 2000, University of Bologna, Italy.

DOI: 10.1039/b003591m

blocks with a range of simple geometries and connectivities. This geometrical diversity together with an enormous knowledge base covering a major fraction of the elements of the Periodic Table can, in principle, be put to use to achieve substantial and widely variable structural control in building a chemically very diverse range of nets. Another attractive feature of using coordinate bond formation for crystal growth is that the process is very often reversible, a factor that we have previously suggested could be crucial in building up ordered networks amenable to single crystal diffraction study.[2] However there is no obvious reason why the link-up chemistry could not be extended to certain reversible C–O, C–N, *etc.* bond forming steps to engineer truly crystalline 2-D and 3-D covalently bonded organic polymers in the form of single crystals.

In recent years my group and others have synthesized and structurally characterised hundreds of coordination framework solids. In some cases the frameworks generate spacious channels and cavities occupied by large amounts of essentially liquid solvent. In others remarkable interpenetrating structures are formed in which the channels created by one framework are filled by one or more independent frameworks which may or may not be identical to the first.[3] This fascinating phenomenon, involving by its very nature infinitely repeated catenane and/or rotaxane interactions, has the potential to provide unique properties arising directly from the ordered entanglement. However, it is desirable also to be able to prevent interpenetration when we wish, and be able to generate, by design, stable structures with large and potentially useful channels. Reports of new interpenetrating systems continue to appear at an ever increasing rate.

Transition metal-based frameworks are particularly interesting because of the possibilities for technologically useful applications that may arise from the special electronic, magnetic, photochemical and catalytic properties shown by these metals and from their capacity, as a consequence of their variable oxidation states, to participate in facile electron transfer. One of the broad aims of our work in this area has been to make a contribution to the foundations upon which true crystal engineering of solids with useful properties will eventually be built. In addition to any useful applications that may be found for these framework materials, they make a significant contribution to basic structural chemistry, representing new geometrical and topological types.

2 Some specific nets

2.1 The diamond net

Of all the possible target nets to aim for when I first started work in the framework area the diamond net seemed the simplest. Accordingly tetra(4-cyanophenyl)methane, L, was synthesized and with Cu^IBF_4 this gave a coordination polymer of composition $LCu(BF_4)\cdot$solvent in the form of single crystals containing precisely the intended infinite diamond-related network with alternating tetrahedral copper and tetrahedral carbon centres as shown in Fig. 1.[4] This result was a considerable confidence booster that the approach to deliberate network construction that was being proposed as having wide applicability extending far beyond merely diamond-like structures was not unrealistic. The solid was unusual in that the ordered network occupied only approximately one third the volume of the crystal, the remaining two thirds being occupied by highly disordered, essentially liquid nitrobenzene together with mobile BF_4^- counter ions. Another early result affording additional confidence that deliberate network design and construction was a realistic possibility was the synthesis and structural characterisation of $[NMe_4][Cu^IZn(CN)_4]$.[2] This also contained, precisely as intended, a single diamond-related network consisting of alternating tetrahedral copper and tetrahedral zinc linked together by linear cyano bridges (Cu–CN–Zn), with NMe_4^+ cations snugly accommodated, by design, in alternate adamantane-like cavities. In contrast to $Zn(CN)_2$ which contains two independent and interpenetrating diamond networks that are electrically neutral, $[NMe_4][CuZn(CN)_4]$ contained, as was the intention of the experiment, only a single anionic network, the required counter cations occupying the spaces where the second framework is found in $Zn(CN)_2$, thereby preventing interpenetration.

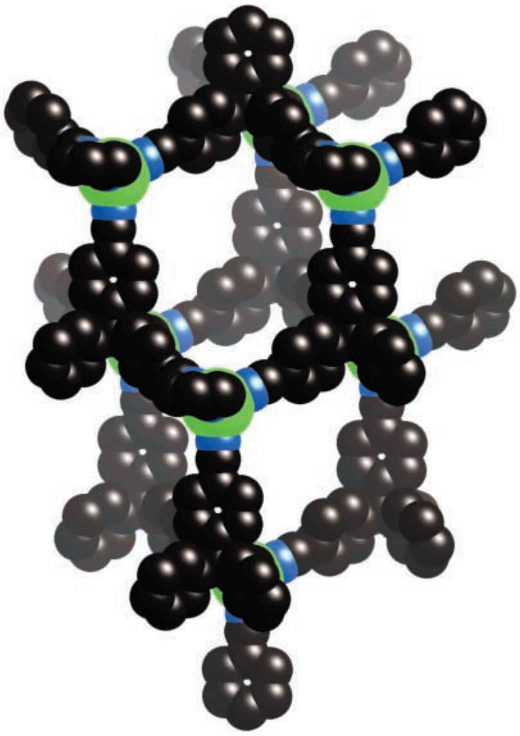


Fig. 1 Two adjacent adamantane-like units within the diamond-like framework formed by tetra(4-cyanophenyl)methane and Cu^I (green).

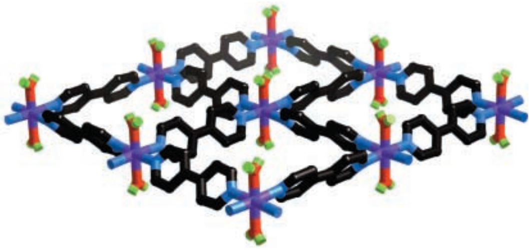


Fig. 2 Four square cavities in a single sheet within the structure of $[Zn(H_2O)_2(4,4'\text{-bipy})_2]SiF_6$.

2.2 The α-Po net

Another very simple target net is the 6-connected α-Po-related net, examples of which, such as the Prussian Blue family of solids, were known before the attempts of my group at deliberate construction. One approach to nets of the α-Po type is to attempt to link together octahedral metal centres by linear 2-connecting ligands, with six ligands attached to each metal and two metals attached to each ligand. A readily available and simple potentially 2-connecting ligand is 4,4′-bipyridine which we used to generate 2-D square grid nets as shown in Fig. 2.[5] Subsequently this ligand and numerous related ones with two pyridine donors have widely been used to generate a variety of 2-D and 3-D nets. However, these pyridine-based 2-connecting ligands seemed inappropriate for the construction of α-Po nets because rarely is it possible that six independent 6-membered N-heterocycles such as pyridines can be accommodated around an octahedral metal centre. By contrast octahedral metal centres readily accommodate six 5-membered N-heterocyclic

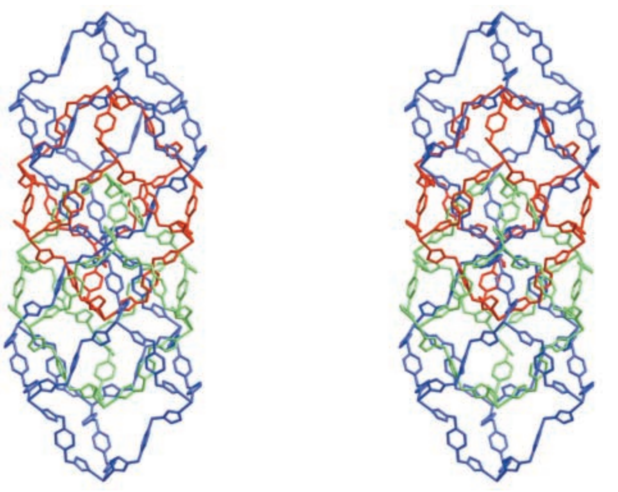
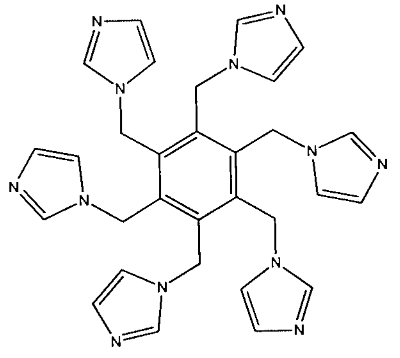


Fig. 3 Stereoview of three interpenetrating independent nets with the α-Po topology in the structure of $Cd(bix)_3(ClO_4)_2$·solvent.

donor ligands such as imidazoles. Therefore 1,4-bis(imidazol-1-ylmethyl)benzene, bix, was synthesized which with $Cd(ClO_4)_2$ gave crystals of composition $Cd(bix)_3(ClO_4)_2$· solvent.[6] This did indeed contain α-Po-related networks. The cavities formed by one network, however, were so large that three independent, interpenetrating networks were observed as shown in Fig. 3. Whilst this work was in progress Mallouk and co-workers reported the construction of an α-Po-related network, somewhat collapsed, using Cd^{2+} as the octahedral centre and 1,4-diaminobenzene as the 2-connector.[7]

Another way in which an α-Po net could possibly be generated is to combine an octahedral metal ion with a ligand having six appropriately disposed donors such as the hexaimidazole species, hkimb, shown in structure **1**. This ligand with CdF_2 affords crystals with rhombohedral symmetry which contain a cationic 3-D network of α-Po-related topology, consisting of alternating 6-connecting cadmium centres and 6-connecting hkimb ligands shown in Fig. 4.[8] The crystals are very heavily hydrated, containing no less than fourteen molecules of water per Cd, none of which however is coordinated. This water assembles itself into two independent and different hydrogen bonded 2-D networks which are woven throughout the 3-D α-Po-related coordination polymer network.



1

2.3 The rutile net

The 6,3-connected net for which rutile can be regarded as the prototype consists of octahedral and trigonal centres in 1 : 2 proportions. One of the simplest potential trigonal 3-connecting ligands is the tricyanomethanide (tcm) ion, $C(CN)_3^-$. This affords highly crystalline "binary" derivatives with divalent metal ions of composition $M[C(CN)_3]_2$. The derivatives of Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg all contain two identical, independent and interpenetrating rutile-related networks as seen in Fig. 5.[9]

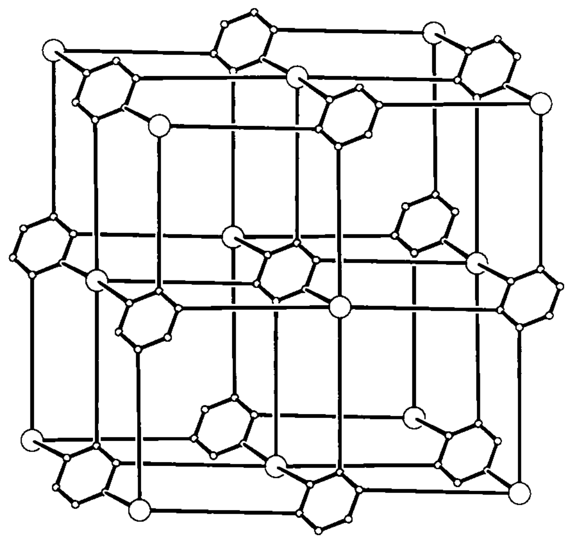


Fig. 4 Schematic representation of the infinite α-Po-like network in $Cd(hkimb)F_2$·$14H_2O$. The imidazolylmethyl links between the Cd and the C_6 rings are represented by heavy lines. Reproduced with permission from ref. 8.

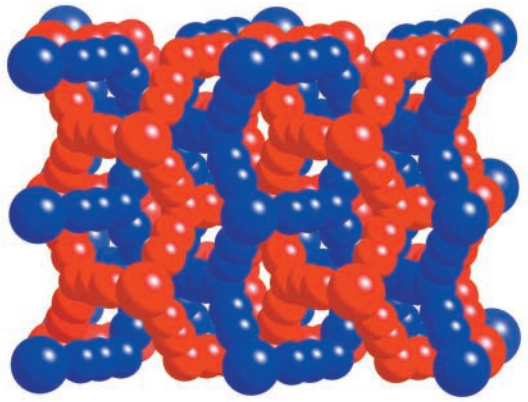


Fig. 5 Two interpenetrating nets with the rutile topology in the structure of $M[C(CN)_3]_2$ (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd or Hg).

Although solvent-free, anhydrous $Co(tcm)_2$ and $Ni(tcm)_2$ are obtained from aqueous solution, the crystals grown from ethanol, generally regarded as a poorer donor for metal ions than water and therefore less likely to interfere in the coordination chemistry, have composition $M(tcm)_2(EtOH)_2$ in which the ethanol is coordinated and the $M(tcm)_2$ network has an entirely different topology.[9] These examples highlight the very fine balance of numerous weak and subtle effects that may determine the structural outcome of framework building reactions: they are paralleled by an earlier observation that although anhydrous crystals of $Cd(CN)_2$ are obtained from aqueous solution, recrystallisation from water containing some Bu^tOH produces crystals that now contain both water and Bu^tOH and possess an entirely different network structure.[10]

2.4 The PtS net

A simple way of linking square planar and tetrahedral centres together, every one attached to four of the other type, is as in the net for which PtS can be regarded as the prototype. In my group the question we asked ourselves was "if we can devise square planar and tetrahedral building blocks with the appropriate functionalities, will they, when combined, spontaneously assemble themselves into a PtS-related network?" We were able to show, with deliberate intent, that square planar $Pt(CN)_4^{2-}$ and tetrahedral Cu^I do indeed spontaneously

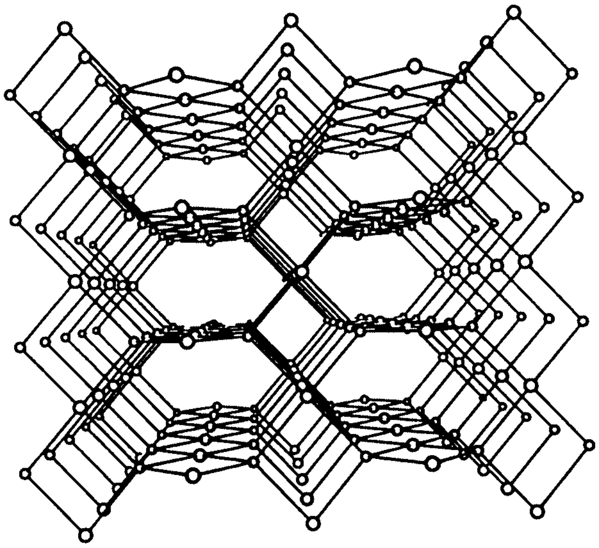


Fig. 6 The anionic PtS-related network seen in the structure of $[NMe_4][Cu^I\{Pt(CN)_4\}]$.

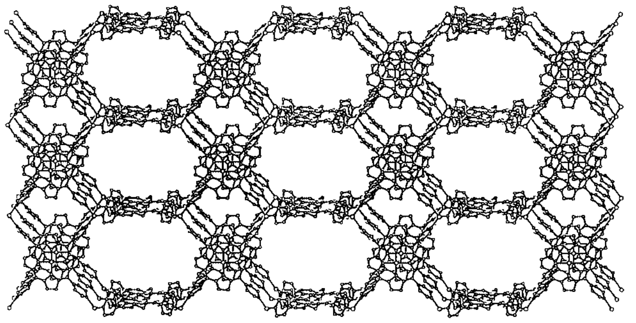


Fig. 7 The cationic $[Cu^I\{Cu^{II}(tpyp)\}]^+$ network with the PtS-related topology (H_2tpyp = 5,10,15,20-tetra(4-pyridyl)porphyrin). Reproduced with permission from ref. 12.

assemble themselves into a network (Fig. 6) with the topology of PtS[11] and further that very much larger square planar porphyrin building blocks with tetrahedral Cu^I or Ag^I do likewise (Fig. 7).[12] The potential of coordination frameworks in general to provide zeolite-like microporous catalysts but with a widely variable and entirely different architecture and functionality was made very clearly evident by these latter porphyrin examples.

The above examples provide encouragement that it will ultimately prove possible to devise building blocks that will spontaneously assemble themselves in much the same way into nets with other chosen topologies, some intriguing and intrinsically simple examples of which are of the Ge_3N_4, Pt_3O_4 and NbO types mentioned earlier.

3 Some highly symmetrical nets from tripyridyltriazine

3.1 Unexpected nets

It has already been pointed out that subtle influences may determine the outcome of framework building reactions and for this reason unexpected results in this field have, in the experience of my group, been not uncommon. Almost always, however, by serendipity, the unanticipated results have been interesting, in some cases outstandingly so. The trigonal bridging ligand 2,4,6-tri(4-pyridyl)-1,3,5-triazine, tpt, shown in structure **2**, is particularly prone to generate unexpected networks, a number of which have been highly symmetrical and intrinsically simple.

With copper(I) perchlorate tpt gives very dark red, almost black crystals of composition $Cu^I(tpt)_{4/3}(ClO_4)$·solvent with cubic symmetry.[13] Two identical independent and interpenetrating 3-D coordination networks are present. An outstanding structural motif, repeated throughout the coordination network, consists of six Cu at the corners of a regular octahedron with alternate triangular faces of the octahedron occupied by μ_3-tpt bridging ligands. Fig. 8 shows two such octahedron-like units sharing one tetrahedral Cu^I. All copper centres are equivalent and of the tetrahedrally coordinated type seen at the centre of Fig. 8 and therefore in the extended network each octahedron-like moiety is attached *via* shared copper(I) "corners" to six identical units. The mode of interpenetration in solvated $Cu^I(tpt)_{4/3}(ClO_4)$, represented in Fig. 9, is such that tpt units occur in close, centrosymmetrically relate pairs, one from each framework. Similar close centrosymmetrically arranged pairs of tpt units are seen in a number of other coordination polymers.

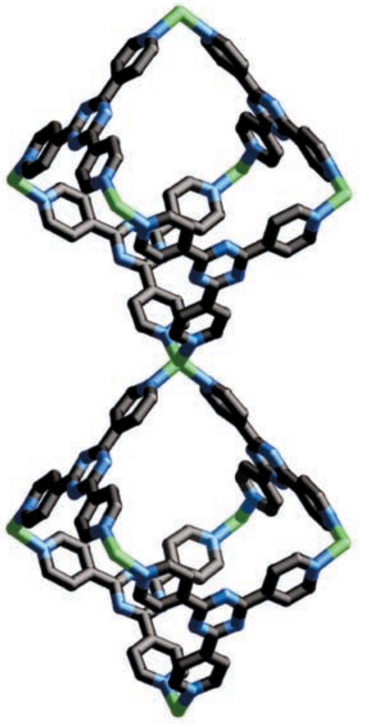
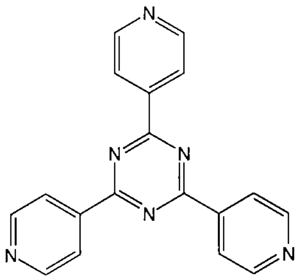


Fig. 8 Two adjacent octahedron-like units linked together by a shared tetrahedral copper(I) in the structure of $Cu^I(tpt)_{4/3}(ClO_4)$. For simplicity only two units are shown here but in the extended network all six copper centres of each unit connect to other units.



tpt

2

3.2 Parallels between coordination polymers and metallosupramolecular arrays

An $M_6(tpt)_4$ assembly, closely similar to those forming part of the infinite polymeric network above, but existing as a discrete molecular species, was reported almost simultaneously by Fujita *et al.*[14] It is interesting that earlier in the development of the two areas, coordination polymers on the one hand and

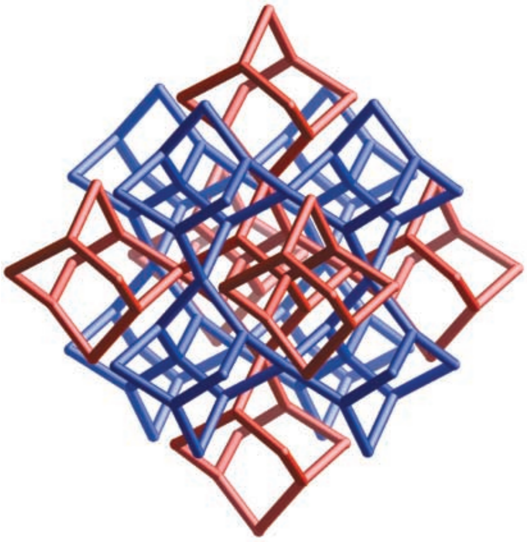


Fig. 9 Two independent interpenetrating networks in the structure of $Cu^I(tpt)_{4/3}(ClO_4)$.

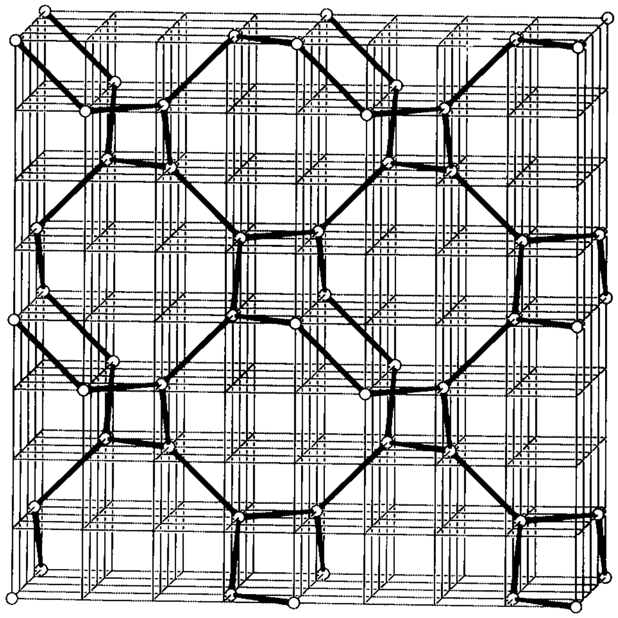


Fig. 10 The chiral (10,3)-a net.

discrete non-polymeric metallosupramolecular arrays on the other, there occurred a similar essentially contemporaneous use of the same ligand, namely, 4,4′-bipyridine, by Fujita *et al.* to generate a molecular $M_4(bipy)_4$ square corral[15] and by my group to generate a square grid polymer[5] containing an infinite 2-D collection of corrals (as seen in Fig. 2) each closely similar to Fujita's molecular version. Fujita was able to demonstrate the incorporation of a number of molecular species inside his molecular square corrals, whereas the analogous square spaces in the infinite 2-D network were occupied (in several derivatives) by an infinite number of identical but perpendicular interpenetrating sheets. In one case however, namely $[Cd(H_2O)_2(bipy)_2][PF_6]_2\cdot 2bipy\cdot 4H_2O$, the square grid sheets did not interpenetrate and each of the square holes was occupied by two non-coordinated 4,4′-bipyridine units.[16]

3.3 The (10,3)-a net

As mentioned earlier, the simplest, most symmetrical 3-connected 3-D net is that designated (10,3)-a, which is shown in its most geometrically regular form (cubic) in Fig. 10. The symbol (*n*,3) is used to characterise the topologies of nets in which all nodes are 3-connecting and where the shortest circuits involving all three different pairs of connections radiating from each node are *n*-gons. Thus in the (10,3)-a net the shortest circuits are all 10-gons as inspection of Fig. 10 will reveal. The "a" indicates this is the most symmetrical of a number of different possible (10,3) nets, which have been catalogued by Wells.[1] This net can be regarded as the 3-connected analogue of the cubic diamond topology that has so dominated 4-connected networks and although it is not familiar at present to many chemists I suspect that it will become commonplace in the years to come. The (10,3)-a net is chiral. Parallel to each of the three crystallographic cubic axes can be seen 4-fold helices which are all of the same hand.

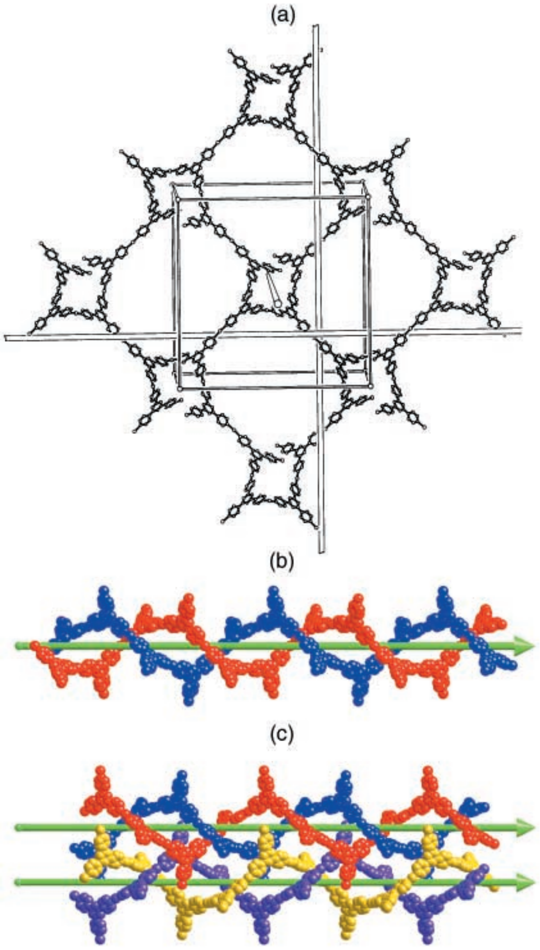


Fig. 11 (a) The C/N/Zn framework of one of the eight cubic (10,3)-a nets present in the structure of $[Zn(tpt)_{2/3}(SiF_6)(H_2O)_2(MeOH)]$. Helices, in this case left handed, running parallel to the three cubic cell axes are highlighted by imaginary "poles" placed along the axes of selected helices. (b) Helical components from two independent nets of the same hand sharing the same helical axis to generate a "double helix". (c) A right handed double helix making multiple π–π contacts with one of the four left handed double helices that are associated with it.

The reaction of tpt with $ZnSiF_6$ yields crystals, again with cubic symmetry, of composition $[Zn(tpt)_{2/3}(SiF_6)(H_2O)_2(CH_3OH)]\cdot$solvent.[17] Networks with the (10,3)-a topology are present. All metal centres are equivalent, with a coordination environment consisting of two *trans* pyridine donors from tpt ligands, one SiF_6^{2-} attached through one F, two water ligands and one methanol. With regard to the connectivity within the infinite network the zinc centres behave as 2-connectors that are almost linear and the tpt components provide the trigonal nodes whereby the (10,3)-a connectivity shown in Fig. 11(a) is generated. There are in fact present eight independent and interpenetrating networks, four right-handed and four left-handed. With regard to the four nets of a given handedness the

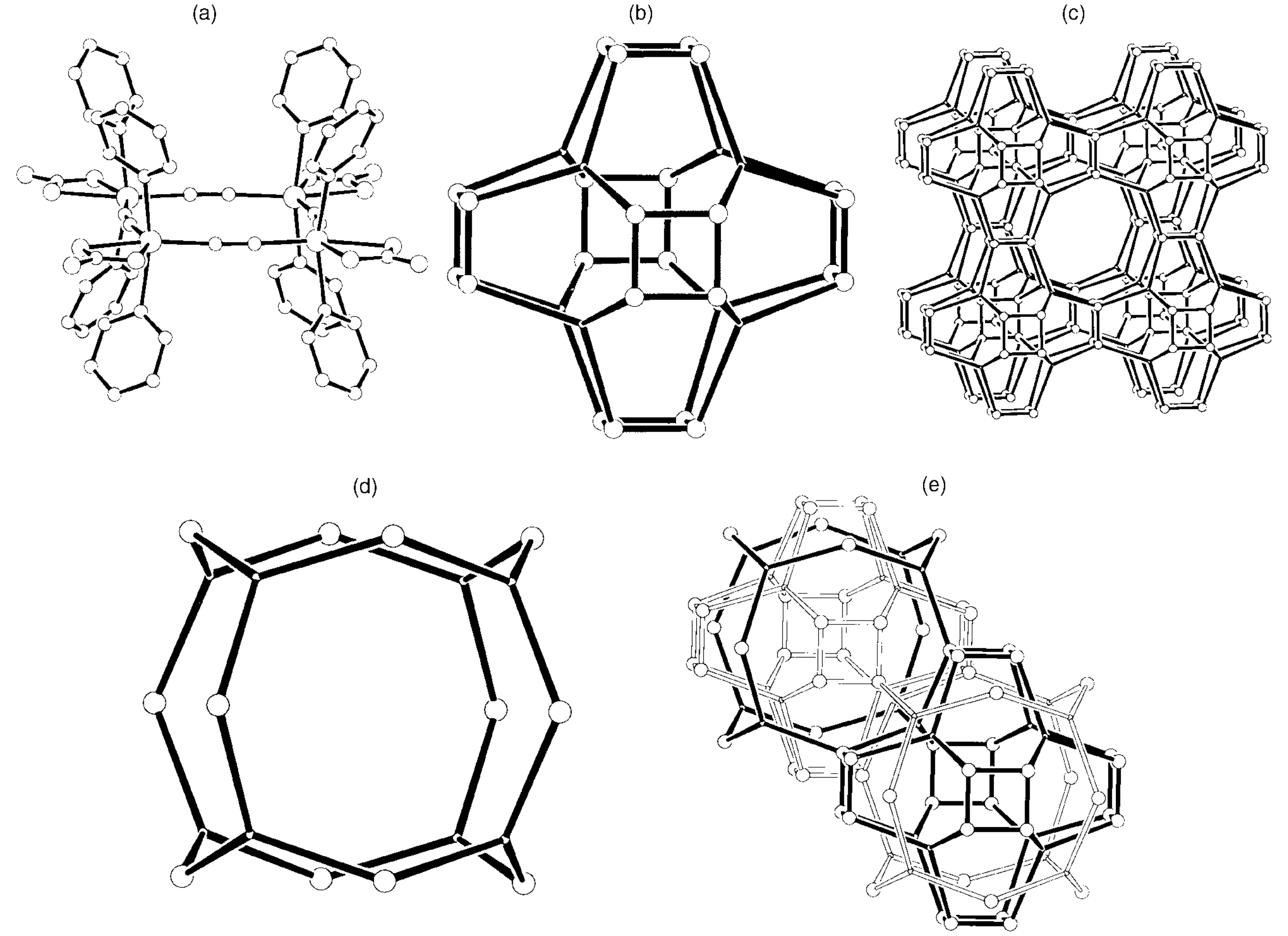


Fig. 12 (a) The zinc coordination environment and the $Zn_4(CN)_4$ "square" components of the structure of $Zn(CN)(NO_3)(tpt)_{2/3}$·solvent. (b) A type A cage. The trigonal centres here represent the centres of the tpt triazine rings and the squares represent the $Zn_4(CN)_4$ units. Chelating nitrate ligands are omitted for clarity. (c) Extended cubic array formed by sharing $Zn_4(CN)_4$ units of the type A cages. (d) A type B cage shown here in isolation, *i.e.* the large cage seen at the centre of the collection of type A cages shown in (c). (e) Mode of interpenetration of two independent nets, 1 and 2, showing the formation of two adjacent sealed-off chambers. A type B cage of net 1 encapsulates a type A cage of net 2 in one chamber and *vice versa* in the adjacent chamber. Reproduced with permission from ref. 18.

second, third and fourth nets are related to the first by half cell translations along the *a*, *b* and *c* directions. A consequence of this is that helices appear in pairs sharing the same helical axis, an example of which is shown in Fig. 11(b). From four nets of a given hand (which we might call nets A, B, C and D), six different pairs (AB, AC, AD, BC, BD and CD) can be formed; running parallel to each of the three cubic axes are found two different pairs of helices, *e.g.* AB and CD pairs parallel to one axis, AC and BD pairs parallel to another and AD and BC pairs parallel to the third. The interpenetration is such that each double helix makes multiple close π contacts (triazine to triazine) with four double helices of the opposite hand, all with their helical axes parallel. In Fig. 11(c) is shown a double helix of one hand making contact, for simplicity, with just one of the four double helices of the opposite hand with which it makes close π–π contact; tpt units, as in the copper(I) case described earlier, appear in close centrosymmetrically related pairs evident in Fig. 11(c).

3.4 A cubic interpenetrating network with extremely large sealed-off chambers

Bringing together tpt, zinc nitrate and cyanide ion produces crystals, once again cubic, with the composition $Zn(CN)(NO_3)(tpt)_{2/3}$·solvent.[18] All zinc centres are equivalent as are all cyanides and all tpt ligands. The metal centres appear at the corners of a square with cyano bridges along the square edges as shown in Fig. 12(a). Bidentate nitrate units are chelated to each zinc, the planar NO_3 units being located in the Zn_4 plane. Each zinc is coordinated above and below this plane by pyridine donors from tpt. Six Zn_4 squares and eight tpt units are linked together as shown in Fig. 12(b) to form a very large and highly symmetrical cage (a type A cage) within which the tpt units are arranged with their centres at the corners of a cube and with their normals directed along the solid diagonals of that cube. Each type A cage is linked *via* shared Zn_4 units to six others to generate an infinite cubic array, part of which is shown in Fig. 12(c). At the centre of the collection of eight type A cages shown in Fig. 12(c) can be seen a much larger cage, a type B cage, which is shown in isolation in Fig. 12(d). The tpt units within the type B cage, like those in the type A cage, are arranged with their centres at the corners of a cube (a much larger cube) and their normals along the cube solid diagonals. There are present in fact two identical and interpenetrating 3-D nets, each of the type shown in Fig. 12(c). The type B cages of one are sufficiently large to encapsulate completely a type A cage from the other. The mode of interpenetration is represented in Fig. 12(e) in which, for simplicity, only two double-shelled chambers are shown. Once again the tpt units appear in very closely associated centrosymmetric pairs, one from each framework. Consideration of van der Waals surfaces reveals that the double shells leave no spaces through which even the smallest molecule could conceivably pass. The chambers, totally sealed off in this way, are exceptionally spacious, being capable of trapping of the order of twenty molecules of solvent, essentially minute, isolated droplets of liquid. A wide range of

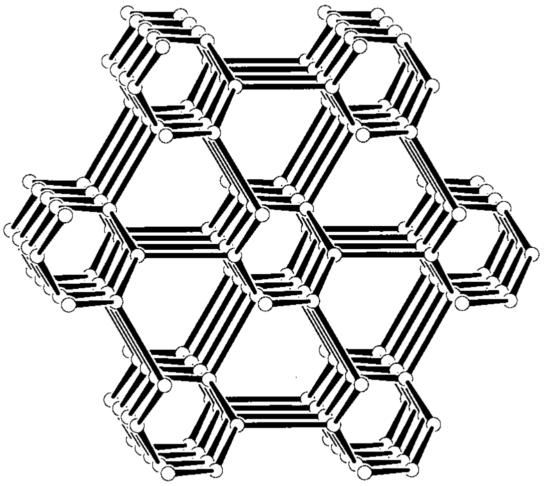


Fig. 13 Representation of the chiral (12,3) net in which all nodes are planar and equivalent. Reproduced with permission from ref. 19.

solvent mixtures can be incorporated; for instance one sample contained on average approximately 18 $CHCl_3$ and 4 CH_3OH molecules per chamber. Thermogravimetric analysis of this particular solid revealed rapid solvent release at 270 °C and no significant loss below ≈250 °C. It is remarkable that solvents as volatile as these can be contained at such temperatures, an indication of the stability and impermeability of the double-shelled enclosures. These circumstances would appear to offer the possibility not only for trapping a range of interesting species but also for conducting microscopic bomb-type experiments both thermal and photochemical. They also raise interesting questions of a philosophical nature regarding how a small group of twenty or so molecules of solvent isolated in this way behaves differently from the same molecules in the corresponding bulk liquid, *e.g.* does the small group of molecules trapped at, say, 240 °C, well above the boiling point at atmospheric pressure have a meaningful and calculable "pressure", a bulk property?

3.5 The (12,3) net

Real chemical examples of 3-connected 3-D nets have been relatively rare to date but, as suggested elsewhere in this article, increasing numbers can be anticipated as coordination polymers start to be more widely studied. When one considers the entire set of (n,3) nets as n increases, an interesting question is "is there an upper limit for n?", or, in other words "what is the 3-D 3-connected net whose shortest circuits are as large as possible?". The chiral (12,3) net shown in Fig. 13 is the one with the largest value of n considered by Wells.[1] The tpt ligand in the coordination polymer $Ni(tpt)(NO_3)_2\cdot$solvent provides the first real chemical example of this exceptional net.[19] Whilst neither strictly trigonal nodes alone nor strictly T-shaped nodes alone can be used to generate the (12,3) net without strain, the net can be constucted in a completely strain-free manner from alternating T and trigonal nodes. This is precisely what is observed in the structure of $Ni(tpt)(NO_3)_2\cdot$solvent a simplified representation of which is shown in Fig. 14. All nickel centres are equivalent, each lying, together with one of its three coordinated pyridyl groups, on a 2-fold axis, the other two pyridyl groups being *cis* to the first and related to each other by the 2-fold axis. The octahedral coordination of the nickel is completed by oxygen atoms from monodentate and bidentate nitrate anions which are disordered around the 2-fold axis. The nickel centres therefore represent the T nodes seen in Fig. 14 and the trigonal nodes are found at the centres of the tpt triazine rings. From the topological point of view the (12,3) net occupies a unique position amongst all the uniform nets in showing self-entanglement such that some of its shortest circuits have other shortest circuits passing through them.

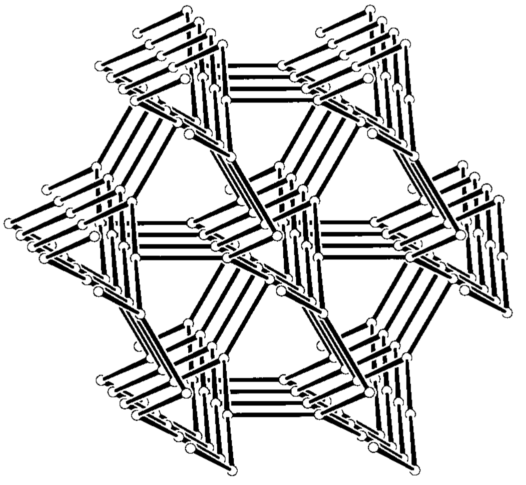


Fig. 14 Representation of the net with (12,3) topology seen in the structure of solvated $Ni(tpt)(NO_3)_2$. The trigonal nodes are located at the centres of the tpt triazine rings and the T-shaped nodes at the Ni. Reproduced with permission from ref. 19.

4 Chelating building blocks

4.1 Potential advantages of chelating building blocks

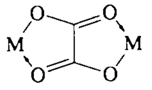
All the networks described so far in this article have involved making bonds between metal centres and monodentate donors at the termini of bridging ligands; it was sensible to start the exploration of a new field with the simpler systems. However, as intimated in an initial paper on framework construction,[2] if building blocks can be devised in which metal centres are bound at chelating sites rather than monodentate sites, not only framework stabilities will be much enhanced by the extremely powerful chelate effect but the number of possible outcomes will be much reduced affording much better structural control in network assembly.

One drawback to the use of ligands with monodentate metal-binding sites arises from the fact that the coordination environment adopted by the metal centre is relatively uncertain. Especially when the solvent and the anion can compete for the metal, the number of ligands per metal and their geometrical arrangement can be very variable and unpredictable. One obvious way to reduce the multiplicity of possible outcomes is to avoid solvents and anions that are likely to compete as ligands, but even then, with ligands providing only monodentate metal-binding sites, coordination number and geometry remain significantly uncertain, as is illustrated by some of the examples above and many others. These uncertainties should be much reduced, possibly in favourable cases eliminated entirely, by the use of well designed ligands that bind metals at chelating sites. The high thermodynamic stability of the association between chelating site and metal, arising from the potent entropy-related chelate effect, should provide effective protection against competitor ligands such as anions, and this should be particularly true if the chelating system itself were anionic. In addition the total number of ligands per metal is reduced and, as a consequence, the scope for alternative outcomes is correspondingly reduced.

The use of chelating units for the construction of infinite networks provides a number of significant bonuses of a geometrical character, over and above the stabilisation flowing from the chelate effect. One of these arises from the fact that when an octahedral metal takes on three ligands bearing bidentate metal binding sites the metal itself, from the point of view of topology, becomes a 3-connector, thereby affording ready and variable access to the little known 3-connected nets. Similarly, when a tetrahedral metal centre takes on two ligands bearing bidentate metal-binding sites the metal becomes a 2-connector with an approximately 90° twist.

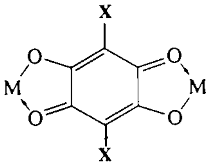
4.2 Oxalate and dihydroxybenzoquinone-based 2-connectors

The oxalate ion is one of the simplest imaginable connecting ligands potentially able to bridge between two metal ions in the bis bidentate chelating manner represented in structure **3**. Its metal derivatives over the years have been the focus of an enormous amount of work. Interestingly, in the coordination polymer networks in which octahedral metal centres are chelated by three oxalates and each oxalate bridges two metal centres, both 2-D hexagonal grid (6,3) nets[20] and 3-D (10,3)-a nets[21] have been observed. Particularly interesting from the net point of view is $[Fe(2,2'\text{-bipy})_3][Fe_2(ox)_3]$ in which the anionic oxalate-bridged network adopts the (10,3)-a topology; within the cavities of the chiral anionic network are found chiral $[Fe(bipy)_3]^{2+}$ counter cations all with the Δ configuration. In the 2-D (6,3) nets the absolute configurations of the metal centres are required to alternate, each Λ centre being surrounded by three Δ centres and *vice versa*, whereas in the (10,3)-a nets the absolute configurations of all the metal centres in the network must be the same.



3

Closely related to oxalate from the point of view of connectivity, charge and the nature of the chelating donor atoms are the bis-bidentate dihydroxybenzoquinone-based dianions, represented in structure **4** ($dhbq^{2-}$ when X = H; chloranilate dianion, can^{2-}, when X = Cl) which also have the potential to act as simple linear 2-connectors. In order to use such 2-connectors to generate a diamond net, an obvious early objective in exploratory work, an 8-coordinate metal would be required and we have found that Y^{3+} is able to play this role, affording with can^{2-} the network with diamond topology shown in Fig. 15. Divalent transition metal cations with can^{2-} generate crystals of composition $M^{II}(can)(H_2O)_2$ (for M = Mn, Fe, Co, Ni or Zn) with a common zig-zag polymeric chain structure shown in Fig. 16.[22] We and others[23] have obtained hexagonal grid sheet polymers of composition $M_2(lig)_3$ with $dhbq^{2-}$ and can^{2-} in which the metal centres have octahedral environments provided by three bidentate, bridging ligands; $dhbq^{2-}$ affords an isostructural series of compounds of composition $M_2(dhbq)_3{\cdot}24H_2O$ (M = Y, La, Ce, Gd, Yb or Lu) containing 2-D hexagonal grid sheets of the type shown in Fig. 17.[24] A particularly favourable hydrogen bonded association of water molecules forming $M_2(H_2O)_{18}$ pentagonal dodecahedral cages, similar to the dodecahedral $(H_2O)_{20}$ cages seen in certain gas hydrates, is located in hexagonal cavities of the network as shown in Fig. 17(b). This stable, preferred cage arrangement appears to be responsible for the common structure seen with trivalent cations of relatively widely differing radius.



4

4.3 3-Connectors based on hexaazatriphenylene

Turning now to 3-connecting chelating ligands bearing a trigonally disposed set of three bidentate metal-binding sites, hexaazatriphenylene, hat, structure **5** and its derivatives have an appealing simplicity and symmetry. Crystals of composition $Ag(hat)X{\cdot}2CH_3NO_2$ ($X = ClO_4$ or BF_4) have the (10,3)-a topology.[25] Each hat ligand chelates three silver centres and each Ag is chelated by three hat ligands as shown in Fig. 18 which represents a portion of the extended (10,3)-a structure. The nitromethane molecules are housed in chiral micropores in the (10,3)-a network in a helical fashion with very close O · · · N contacts. Significantly, nitromethane can be replaced by water not only with retention of framework integrity but also with retention of single crystal character! testament to the effectiveness of the chelating tactic for reinforcing networks. Acentric assemblies such as this are not common and may find applications as second order non-linear optical materials.

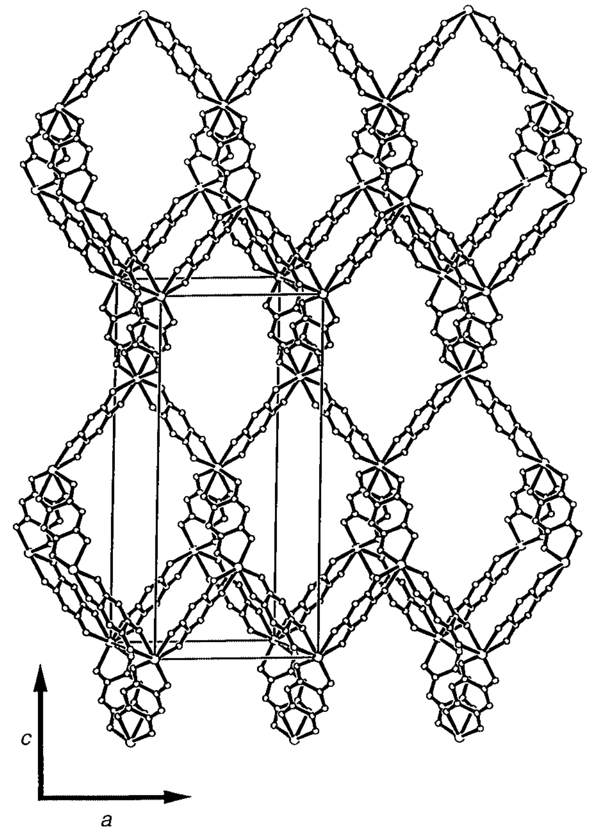


Fig. 15 The anionic $Y(can)_2^-$ net with diamond-like topology. Chlorine atoms of the can units have been omitted for clarity. Each bis-bidentate can^{2-} acts as a 2-connector between 8-coordinate Y which provide the 4-connecting nodes of the net. The fine lines indicate the body centred unit cell.

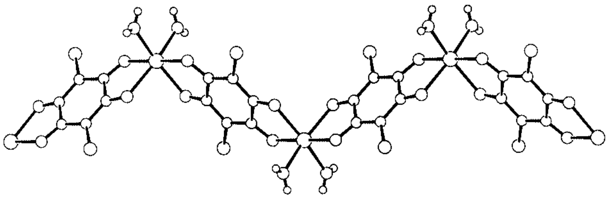
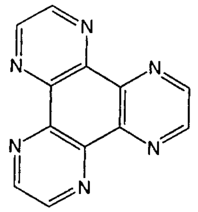


Fig. 16 The 1-D zig-zag polymeric structure of $[Fe^{II}(can)(H_2O)_2]{\cdot}H_2O$.



5

Crystals of composition $Ag(hat)(ClO_4){\cdot}4.5H_2O$ grown from hot water (≈90 °C) are hexagonal and although every hat ligand binds three silver centres and every Ag binds three hat ligands as in the nitromethane-solvated example above, the topology

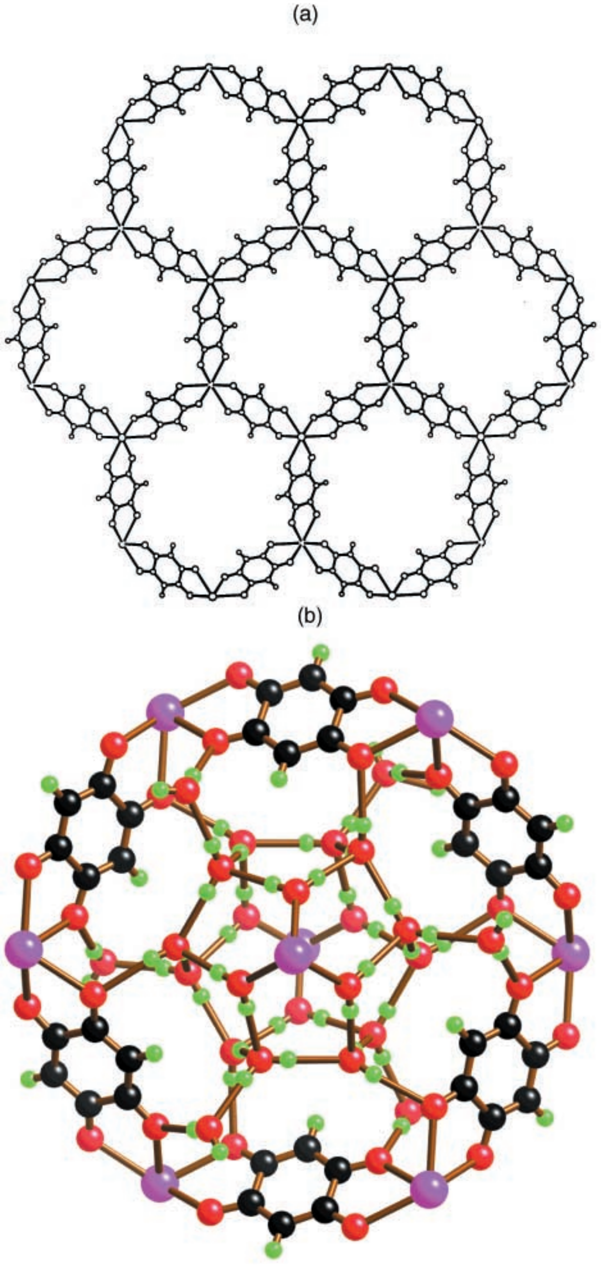


Fig. 17 (a) Structure of a $[Ce_2(dhbq)_3]_n$ sheet. (b) Representation of a $Ce_2(H_2O)_{18}$ cage passing through a $Ce_6(dhbq)_6$ ring.

is quite different, namely, that of the (8,3)-b net.[1] Metal–hat coordination networks with other topologies have been discovered in recent work. Also in current work a substituted hat derivative, which is sterically prevented from forming a tris association with Ag^I and forms only a bis association, affords a greatly "expanded" (10,3)-a net occupying a volume per hat unit close to eight times that seen in $Ag(hat)X{\cdot}2CH_3NO_2$. In the unsubstituted hat case the silver centre is able to bind three chelating ligands and to act as a trigonal 3-connector in the (10,3)-a net, but in the case of the sterically blocked hat the tetrahedrally bis-chelated Ag acts as a linear 2-connector so that the separation from trigonal node to trigonal node is almost exactly doubled. The resulting (10,3)-a net is so much more open that two interpenetrating nets of opposite hand are observed. This provides a very nice example of the way in which tinkering with the ligand can afford substantial structural control; we did anticipate and hope for precisely the structure observed but in no way could it have been guaranteed.

$Cd(ClO_4)_2$ with hat gives a 3-connected net (of unprecedented topology) in which both ligand and metal provide 3-connecting nodes. $Cd(NO_3)_2$ on the other hand gives a 1D zigzag polymer in which both ligand and metal act as 2-connectors. In the nitrate case the more strongly coordinating anion interferes in the coordination chemistry and competes successfully with the third chelating bay of hat for coordination to the metal. Presumably as one adds dipositive cations to successive chelating sites of the electrically neutral hat ligand the affinity for cations at the remaining sites decreases. This suggests that triply chelating ligands with an overall negative charge may be better able to bind three cations and may provide more stable 3-connected coordination polymers than hat. A number of such ligands are under current investigation.

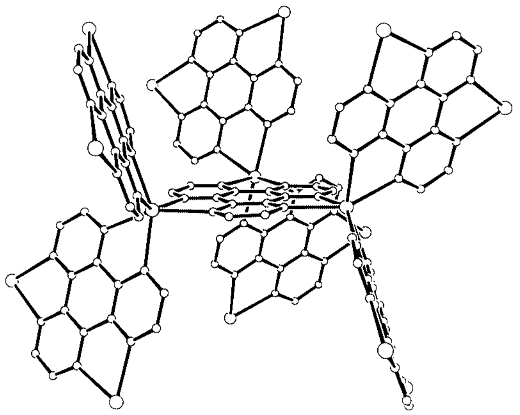


Fig. 18 A segment of the Ag/hat framework in $[Ag(hat)(ClO_4)]{\cdot}2CH_3NO_2$. Reproduced with permission from ref. 25.

5 Concluding remarks

A number of the examples presented above provide confidence that the deliberate net-based approach to framework building has a lot to offer. We doubt that any level of theory available now or in the immediately foreseeable future could have predicted, simply on the basis of the components present in the reaction mixture, the remarkable tpt-based network structures described and the same can be said of many other network-forming reactions. Relatively weak interactions between framework and large numbers of often highly dynamic solvent molecules appear to be important if not decisive in some cases; these interactions would not be easy to model. Connecting ligands that bind metal centres **strongly and predictably** at chelating sites would appear to offer large tracts of virgin territory for exploration, promising not only improved structural control in network assembly but also mechanically and chemically more robust structures. At this stage, experimentation, often of the most simple type, promises to continue to be a very fruitful way forward and many exciting surprises undoubtedly remain in store.

Acknowledgements

The author is extremely grateful to the Australian Research Council, the Selby Scientific Foundation and the American Chemical Society Petroleum Research Fund for support and to the following colleagues, collaborators and research students: Dr B. F. Hoskins, Dr B. F. Abrahams, Dr S. R. Batten, Dr Patricia Jackson, J. Coleiro, S. Egan, H. Hamit, Dr D. A Slizys, Dr R. W. Gable and Dr D. Michael. Special thanks are due to Dr Abrahams for invaluable assistance with the figures.

References

1 A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley-Interscience, New York, 1977.
2 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.
3 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
4 B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 5962.
5 R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 1677.

6 D. A. Slizys, B.Sc.(Hons) Thesis, University of Melbourne, 1993.

7 C. M. Bell, S. W. Keller, V. M. Lynch and T. E. Mallouk, *Mater. Chem. Phys.*, 1993, **35**, 225.

8 B. F. Hoskins, R. Robson and D. A. Slizys, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 2752.

9 S. R. Batten, B. F. Hoskins and R. Robson, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 445; *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2977.

10 B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 60.

11 R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 762.

12 B. F. Abrahams, B. F. Hoskins, D. M. Michael and R. Robson, *Nature* (*London*), 1994, **369**, 727.

13 B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 1690.

14 M. Fujita, D. Oguro, M. Miyazawa, K. Oak, K. Yamaguchi and K. Ogura, *Nature* (*London*), 1995, **278**, 469.

15 M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645.

16 R. W. Gable, B. F. Hoskins and R. Robson, 201st National Meeting of the American Society, Division of Inorganic Chemistry, Atlanta, Georgia, April 14–19, 1991.

17 B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 1313.

18 S. R. Batten, B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1995, **117**, 5385.

19 B. F. Abrahams, S. R. Batten, M. J. Grannas, H. Hamit, B. F. Hosins and R. Robson, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1475.

20 R. Pellaux, H. Schmalle, R. Huber, P. Fisher, T. Hauss, B. Ouladdiaf and S. Decurtins, *Inorg. Chem.*, 1997, **36**, 2301; C. Mathoniere, C. J. Nuttal, S. G. Carling and P. Day, *Inorg. Chem.*, 1996, **35**, 1201; J. Larionova, B. Mombelli, J. Sanchiz and O. Kahn, *Inorg. Chem.*, 1998, **37**, 679.

21 S. Decurtins, H. W. Schmalle, P. Schneuly and H. R. Oswold, *Inorg. Chem.*, 1993, **32**, 1888.

22 B. F. Abrahams, K. D. Lu, B. Moubaraki, K. S. Murray and R. Robson, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 1793.

23 A. Weiss, E. Riegler and C. Robl, *Z. Naturforsch.*, *Teil B*, 1986, **41**, 1501.

24 B. F. Abrahams, J. Coleiro, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 603.

25 B. F. Abrahams, P. A. Jackson and R. Robson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2656.